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# Full Four-Component Relativistic Calculations of NMR Shielding and Indirect Spin–Spin Coupling Tensors in Hydrogen Halides

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**ABSTRACT:** Various methods for the inclusion of relativistic effects in the calculation of NMR parameters are discussed. Benchmark values for the NMR shieldings and indirect nuclear spin–spin coupling tensors for the hydrogen halides are calculated using the four-component relativistic random phase approximation method. Apart from recovering the well-known trend of increasing hydrogen isotropic shielding going from HF to HI, we also find a large effect on the anisotropy that decreases along this series. Inclusion of spin-orbit coupling in a nonrelativistic formalism suffices to recover both effects on the hydrogen shieldings but fails to reproduce the much larger effect on the halogen shieldings. This effect can be explained by considering the relativistic mass-velocity operator that contains correction terms to the nonrelativistic magnetic field operators. We recommend routine inclusion of the one-electron spin-orbit correction in calculations of hydrogen shieldings for hydrogens bonded to heavy atoms. For the heavy nucleus shielding one should include an additional

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mass-velocity correction. The relativistic effect on the indirect nuclear spin–spin coupling tensor is large and affects mainly the isotropic values; the effect on the anisotropy is small. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1262–1273, 1999

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## Introduction

Relativity has a profound influence on the electronic wave function in molecules that contain heavy elements. While changes in the valence region can often be modeled by introducing extra or modified operators in a one-component nonrelativistic formalism, use of the full four-component relativistic Dirac equation may be necessary for molecular properties that depend on the value of the wave function near the nuclei. An example of such molecular properties is the set of parameters that is used in the effective Hamiltonian for NMR spectroscopy. In a previous article<sup>1</sup> we considered the relativistic calculation of electric field gradients at the nuclei in the hydrogen halides; in this article we report NMR shieldings and indirect nuclear spin–spin couplings for these molecules.

Ramsey<sup>2</sup> neglects spin-orbit effects in his landmark 1950 article on chemical shieldings. However, the increased precision of experimental techniques and the advent of sophisticated *ab initio* theory have made it possible to investigate the observed shieldings in more detail and include effects that were not included in the effective Hamiltonian introduced by Ramsey.<sup>2</sup> The effect of relativity on the chemical shieldings has become a subject of great interest lately. A number of methods have been developed to take relativistic effects into account at various levels of approximation. Among the different relativistic effects, spin-orbit coupling is of particular importance for the chemical shieldings because it gives rise to contributions from the triplet spin-dipolar (SD) and Fermi contact (FC) terms that do not contribute in the usual nonrelativistic second-order perturbation theory formalism.

The first approaches that accounted for the spin-orbit effect used semiempirical wave functions. In 1973 Morishima et al.<sup>3</sup> presented a qualitative explanation of the effect of spin-orbit

couplings on the hydrogen chemical shift in the hydrogen halides that we treat in the present work. Other contributions come from Pyykkö et al.<sup>4</sup> who gave qualitatively correct descriptions of relativistic effects for a range of halogen-containing molecules based on the relativistic extended Hückel method REX.

In order to get quantitative accuracy and to give the computational methods predictive power, more sophisticated techniques need to be used. A convenient method that enables one to use most of the machinery of nonrelativistic *ab initio* quantum chemistry is to introduce relativity via additional perturbative operators, representing to order  $\alpha^2$  (with  $\alpha$  as the fine structure constant) the most important corrections: spin-orbit coupling, the mass-velocity correction, and the Darwin correction. The latter two are usually called scalar relativistic corrections because they may be used in a spin-free formalism. The spin-orbit coupling is important for shieldings and, because these NMR parameters are of more practical interest than spin–spin couplings, its inclusion in shielding calculations has attracted the most attention. In a nonrelativistic formalism for the calculation of NMR shieldings and spin–spin couplings the effect of spin-orbit coupling can be introduced via third-order perturbation theory, using either an analytic formalism or a finite field procedure for one or more of the operators.

Nakatsuji et al.<sup>5</sup> include both the one-electron term of the Breit–Pauli spin-orbit operator and the external magnetic field as finite perturbations in a complex unrestricted Hartree–Fock (HF) method. The components of the shielding tensor are then calculated as expectation values of the nuclear magnetic field operator. Fukui et al.<sup>6,7</sup> point out that this approach cannot be gauge invariant because the spin-orbit interaction operator has been derived without taking into account the vector potentials arising from both the external and nuclear magnetic field. They derive additional contributions by starting from the Breit–Pauli Hamiltonian with an external magnetic field and give a

final expression that is gauge invariant to fourth order in the fine-structure constant. To obtain this gauge-origin invariant result in practice, one furthermore needs to use a complete basis set or use London orbitals as in the nonrelativistic approaches. Another extension of the method of Nakatsuji et al.<sup>5</sup> was presented by Ballard et al.<sup>8</sup> who added a scalar relativistic operator to the zeroth-order Hamiltonian. They used the variationally stable one-electron operator as proposed by Hess,<sup>9</sup> but still in conjunction with the Breit–Pauli spin-orbit operator.

Treating a magnetic field or spin-orbit operator via finite field methods has the disadvantage that it becomes necessary to use complex arithmetic in the self-consistent field (SCF) procedure. Malkin et al.<sup>10</sup> circumvented this problem by using the FC operator as a real finite field perturbation operator. Using an approximate density functional sum over states (SOS-DFPT) method the shielding tensors can then be calculated in a straightforward manner. They omit the SD term and also the FC-II term introduced by Fukui et al.<sup>6,7</sup> While the first term is documented to be small for a wide range of molecules, the second term was found to be significant for the hydrogen halides that Fukui et al.<sup>6,7</sup> treated.

However, the use of singular operators beyond third-order perturbation theory (i.e., beyond first order in the relativistic corrections) presents, in principle, a serious disadvantage of all of these methods. Kutzelnigg<sup>11</sup> showed that the derivation of the FC operator from the nonrelativistic Lévy–Leblond equation<sup>12</sup> with a point magnetic dipole is only valid for use in first-order perturbation theory. The finite field procedure is supposed to mimic first-order perturbation theory but will, because of the finite size of the perturbation strength, include higher order terms as well. The same argument holds for the use of the Breit–Pauli spin-orbit operator in variational calculations. Here the problem is worse because one usually takes the true strength of the spin-orbit operator instead of an arbitrary small scaling parameter. This can make a variational finite field treatment numerically unstable, especially in large basis sets with tight functions that are needed to reach the HF limit in the description of the wave function in the vicinity of the nuclei. The calculations presented so far with these finite field approaches do not seem to show this problem in practice, however.

A better way would be to use the nonsingular spin-orbit operator obtained in the Douglas–Kroll–Hess<sup>9,13</sup> method, but to our knowledge this

route has not yet been taken. One can also use the Breit–Pauli spin-orbit operator in analytic third-order perturbation theory or, equivalently, in quadratic response theory. Here the higher order combination of the singular spin-orbit operator with itself is avoided, although the combination with the FC operator might give problems as well. This method was applied by Kirpekar et al.<sup>14</sup> to the NMR spin–spin coupling parameters of the methane analogues ( $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$ ,  $\text{SnH}_4$ ). In the case of NMR spin–spin coupling tensors no new terms representing the nuclear spin are introduced upon considering a spin-orbit operator because both the FC and the SD terms already contribute in second-order perturbation theory. Kirpekar et al.<sup>14</sup> found only small effects upon inclusion of the spin-orbit operator and no problems with divergences due to the combination of the FC and spin-orbit operator. Inclusion of scalar relativistic effects was, however, not possible in this fashion because of divergences upon combining the Darwin and the FC operator that both have a delta-function dependence near the nuclei. The quadratic response approach is easily generalized to handle shieldings. One then needs to calculate the response of the FC and SD terms to perturbations due to the external magnetic field and the spin-orbit operator. This approach was followed by Vaara et al.<sup>15</sup> in their recent work on the  $^1\text{H}$ ,  $^{13}\text{C}$ , and halogen shielding tensors of the hydrogen and methyl halides. In the present work we use the same method to analyze our four-component results.

Apart from the spin-orbit term, one can also include scalar relativistic effects in a number of ways. By including the vector potential in the derivation of the Breit–Pauli mass-velocity operator as suggested by Fukui et al.<sup>6,7</sup> one obtains a different form of the mass-velocity operator than when applying minimal substitution to the mass-velocity operator derived without the vector potential. This more rigorous procedure then gives rise to additional second-order terms (FC-IV, SD-IV) that are usually not included in NMR shielding calculations. Because these terms contain only one singular operator, they can be evaluated without problems using the linear response formalism. Despite this computational simplicity, the FC-IV and SD-IV terms seem to have been overlooked in most calculations. In a later article Fukui and Baba<sup>16</sup> also discuss the mass-velocity correction within the Douglas–Kroll formalism, but there they use the nonrelativistic magnetic operators in conjunction with a Douglas–Kroll wave function. This

neglect of picture change makes that procedure less well founded than their original approach, even though the Douglas–Kroll method is in principle superior to the Breit–Pauli perturbation approach.

The mass-velocity and Darwin terms also give rise to higher order effects due to the induced relativistic contraction of the wave function. The simplest way to model this effect is to take the relativistic contraction of the *s* shells into account by scaling the FC integrals with a factor obtained from the hydrogenic atom with the appropriate charge.<sup>17</sup> This method can in principle be applied to both the NMR shielding tensor and the NMR spin–spin coupling tensor, but it has mostly been used for the latter property.<sup>18</sup> A more rigorous approach is to include a scalar relativistic correction in the zeroth-order Hamiltonian or to use perturbation theory and treat the operator via third-order perturbation theory. The first alternative is again in principle only possible with non-singular operators. In practice both the singular mass-velocity and Darwin operators and the variationally stable nonsingular Douglas–Kroll operators have been used in variational calculations. Sometimes only these scalar relativistic corrections have been included, as in the work of Schreckenbach and Ziegler<sup>19</sup> who use the density functional theory (DFT) method with the mass-velocity and Darwin operators in the zeroth-order Hamiltonian. Both scalar and spin-orbit corrections are used in a recent generalization of this DFT approach by Wolff and Ziegler,<sup>20</sup> where they also add the one-electron spin-orbit operator to the zeroth-order Hamiltonian. In both cases precautions like the use of a frozen core are taken due to the singular character of the operators used.

We see that all of the approximate relativistic methods involve a rather complicated formalism that may suffer from singularities in both the variational and perturbational approach. In the latter case one should go to third or even fourth order to obtain all the contributions. Another complication is that one should also pay attention to the picture change inherent in approximate relativistic methods and the convergence of the perturbation approach itself. Both aspects have not been thoroughly investigated in this context so far. An alternative to approximate relativistic approaches, which can also serve to benchmark the methods, is to start directly from the four-component relativistic Dirac equation and calculate the NMR shieldings and spin–spin couplings via second-order perturbation theory expressions. A finite perturba-

tion theory approach based on the Dirac–HF (DHF) method was recently used by Ishikawa et al.<sup>21</sup> to calculate shieldings for the noble gas atoms, the hydrogen molecule, and the two lightest hydrogen halides. Their approach does not suffer from problems with singular operators because the external magnetic field may be chosen as the finite perturbation and no operators with an  $r^{-3}$  dependency occur in the variational part of the calculation. A disadvantage is that the DHF wave function needs to be determined using an unrestricted HF method because the finite magnetic perturbation breaks the time-reversal symmetry of the Hamiltonian. This increases the computational cost of the DHF method. Another method was proposed by Quiney et al.,<sup>22</sup> who used an approximate SOS method of uncoupled HF with orbital energy differences as excitation energies. While their method is made gauge invariant, it suffers from inaccuracies due to the approximate nature of their response formalism.

We use analytic second-order perturbation theory as formulated in the relativistic random phase approximation (RPA) method.<sup>23</sup> Apart from the proper treatment of relativity, the advantage of this formalism lies in the fact that we need to calculate only one type of response function and, if we neglect the contribution of positronic states in the response function,<sup>24</sup> possibly one expectation value for the diamagnetic contributions. Below we outline the formalism based on the relativistic variant of the RPA method that we previously applied to frequency dependent polarizabilities.<sup>25</sup>

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## Theory

The four-component relativistic equivalent of the HF method is the DHF method. Here the one-electron part of the Hamiltonian is given by the relativistic Dirac Hamiltonian while the electron–electron interaction is represented by nonrelativistic instantaneous Coulomb interaction. The description of the electron–electron interaction may be improved by adding either the Gaunt interaction or the full Breit interaction. We use only the Coulomb term. The calculations of Ishikawa et al.<sup>21</sup> showed that the effect of the Breit interaction reduces the shielding by less than 0.2% for their heaviest atom Xe.

When we have obtained the DHF wave function we can consider the effect of additional interaction terms in the Hamiltonian using response theory. A

relativistic generalization of the RPA method, where we consider the effect of two perturbing magnetic field operators, then gives us the possibility of calculating both NMR spin–spin coupling and NMR shieldings as zero-frequency linear response functions (operators given in their second quantized form).<sup>23,26</sup>

$$J_{\mu\nu}(M, N) = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2}{h} \gamma_M \gamma_N (ec)^2 \langle \langle \frac{(\boldsymbol{\alpha} \times \mathbf{r}_M)_\mu}{r_M^3}; \frac{(\boldsymbol{\alpha} \times \mathbf{r}_N)_\nu}{r_N^3} \rangle \rangle_{E=0} \quad (1)$$

and

$$\sigma_{\mu\nu}(M) = \left( \frac{\mu_0}{4\pi} \right) (ec)^2 \langle \langle \frac{(\boldsymbol{\alpha} \times \mathbf{r}_M)_\mu}{r_M^3}; (\boldsymbol{\alpha} \times \mathbf{r}_G)_\nu \rangle \rangle_{E=0}. \quad (2)$$

The shielding tensors calculated in this way are not gauge-origin independent as can be seen from eq. (2), where the shielding tensor depends on the gauge origin  $G$ . A gauge-origin invariant expression may be derived using London orbitals. For large basis sets the gauge dependence should not be severe and can be tested by varying the gauge origin and the size of the basis set. In our calculations we present results with the gauge placed at the position of the halogen nucleus, but we also tested other options (see below).

The time consuming part of the calculation after the unperturbed wave function has been obtained is the iterative solution of the coupled HF equation. If we want to calculate the complete spin–spin coupling tensor the shielding tensors may be obtained at minimal extra cost because no additional coupled HF equations need to be solved. In relativistic calculations one may obtain the diamagnetic terms in two ways by including electron–positron rotations explicitly in the response calculation or by making the Sternheim approximation<sup>27</sup> and calculating the expectation value of the diagonal four-component diamagnetic spin-orbit operator. The first method seems more rigorous from a methodological point of view but relies on the quality of sampling of the positronic orbital space in a finite basis. Calculation of the diamagnetic contributions to indirect nuclear spin–spin coupling constants using both methods show that the results of both approaches are very close, but that the expectation value method is less sensitive to the basis set employed.<sup>24</sup> We therefore used the expectation value method in the present work.

For comparison we also used a nonrelativistic approach<sup>15</sup> in which we studied the effect of spin-orbit coupling on the shieldings by evaluating the quadratic response functions

$$\sigma_{\mu\nu}^{\text{FC}}(M) = \left( \frac{e^2}{2m} \right) \left( \frac{\mu_0}{4\pi} \right) \times \langle \langle A_\mu^{\text{FC}}(M); B_\nu^{\text{OZ}}(G), H^{\text{SO1}} + H^{\text{SO2}} \rangle \rangle_{0,0} \quad (3a)$$

and

$$\sigma_{\mu\nu}^{\text{SD}}(M) = \left( \frac{e^2}{2m} \right) \left( \frac{\mu_0}{4\pi} \right) \times \langle \langle A_\mu^{\text{SD}}(M); B_\nu^{\text{OZ}}(G), H^{\text{SO1}} + H^{\text{SO2}} \rangle \rangle_{0,0} \quad (3b)$$

with

$$A_\mu^{\text{FC}}(M) = \frac{4\pi g_e}{3} \delta(\mathbf{r}_M)(\mathbf{s})_\mu \quad (3c)$$

(FC),

$$A_\mu^{\text{SD}}(M) = \frac{g_e}{2} \frac{3(\mathbf{r}_M \cdot \mathbf{s})(\mathbf{r}_M)_\mu - r_M^2(\mathbf{s})_\mu}{r_M^5} \quad (3d)$$

(SD),

$$B_\nu^{\text{OZ}}(G) = (\mathbf{l}_G)_\nu \quad (3e)$$

(orbital Zeeman),

$$H^{\text{SO1}} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2m^2c^2} \sum_K \frac{Z_K(\mathbf{l}_K \cdot \mathbf{s})}{r_K^3} \quad (3f)$$

(Breit–Pauli one-electron spin orbit), and

$$H^{\text{SO2}} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2m^2c^2} \frac{\mathbf{l}_{12} \cdot (\mathbf{s}_1 + 2\mathbf{s}_2)}{r_{12}^3} \quad (3g)$$

(Breit–Pauli two-electron spin orbit). As observed by Fukui et al.,<sup>6,7</sup> this formulation is not gauge-origin invariant and lacks a number of additional terms. Because we are comparing to a four-component formalism, which also lacks gauge-origin invariance in the present formulation, this gauge-origin invariance is not our primary concern for the present application. The terms DS-II, ROO, OP-III, and OP-IV defined by Fukui et al.<sup>6,7</sup> arise from the Breit interaction and are not taken into account in our four-component formalism either, so they should not be included here.

The perturbation approach is supplemented by calculation of the scalar relativistic FC-IV and SD-IV terms of Fukui et al.<sup>6</sup> via linear response theory

$$\sigma_{\mu\nu}^{\text{MV}}(M) = \left( \frac{e^2}{2m} \right) \left( \frac{\mu_0}{4\pi} \right) \langle\langle A_{\mu}^{\text{FC}}(M) + A_{\mu}^{\text{SD}}(M); B_{\nu}^{\text{MV}} \rangle\rangle_0 \quad (4)$$

with

$$B_{\nu}^{\text{MV}} = \frac{p^2}{8m^3c^2}(\mathbf{s})_{\nu} \quad (4a)$$

(mass velocity external field).

The shielding tensors of a linear molecule can be represented in terms of the isotropic  $\sigma(=1/3\sigma_{\parallel} + 2/3\sigma_{\perp})$  and anisotropic  $\Delta\sigma(=\sigma_{\parallel} - \sigma_{\perp})$  shielding parameters, where  $\parallel$  and  $\perp$  indicate components of the shielding parallel and perpendicular to the molecular bond, respectively. The combination of the mass-velocity external-field and FC operators (MVEF-FC) only contributes to the isotropic shielding parameter, and the combination of the MVEF and SD operators (MVEF-SD) only contributes to the anisotropic shielding parameter.

A similar representation is used in the discussion of the indirect nuclear spin-spin coupling tensor where the isotropic parameter  $J(=1/3J_{\parallel} + 2/3J_{\perp})$  and the anisotropic parameter  $\Delta J(=J_{\parallel} - J_{\perp})$  are defined. We also find it convenient to use the reduced coupling constants  $K$  that are related to  $J$  via<sup>28</sup>

$$K(M, N) = \frac{h}{\hbar^2 \gamma_M \gamma_N} J(M, N). \quad (5)$$

## Computational Details

The nonrelativistic linear and quadratic response calculations were carried out using the Dalton<sup>29</sup> code. The relativistic RPA calculations were carried out using the DHF method based on the four-component Dirac-Coulomb Hamiltonian using the program Dirac.<sup>30</sup> In the shielding calculations we used the common gauge-origin formalism with the gauge origin placed on the halogen nucleus. In addition, we used the London orbital formalism in nonrelativistic calculations to test the gauge-origin dependence of the calculated shieldings. The calculations were performed using the experimental equilibrium geometries from Huber and Herzberg,<sup>31</sup> except for HF where we used the

geometry from the numerical calculation of Sundholm et al.<sup>32</sup> The basis sets used were uncontracted and they were the same as those used in the finite field CCSD(T) EFG calculations in our previous article.<sup>1</sup> The basis sets for bromine and iodine basis sets were relativistically optimized using the even tempered generating formula for bromine and iodine and the basis sets for fluorine, chlorine, and hydrogen were essentially the uncontracted cc-PVTZ basis sets of Dunning and Woon.<sup>33,34</sup> In the relativistic calculations an (isotropic) Gaussian charge distribution<sup>35</sup> was used to model the finite size of the nuclei in the calculation of the electrostatic electron-nucleus interaction integrals. However, for the interaction with the magnetic moment of the nuclei we modeled the nucleus as a point magnetic dipole.

## Results and Discussion

### SHIELDING TENSORS

The calculated values are not invariant to the choice of gauge origin. To estimate the dependence of the results on this choice of origin, we compared the nonrelativistic parameters with a calculation in which the London orbital formalism is used (Table I). If we place the gauge origin on the hydrogen nucleus we get a large deviation from the London orbitals results, especially for the hydrogen shieldings. Test calculations show that this gauge dependence is largely due to the lack of tight halogen d functions in the virtual space, which causes an underestimation of the paramagnetic contribution when the gauge origin is placed on the hydrogen atom. This gives an incomplete description of the gauge term, because the diamagnetic term is evaluated via an expectation value and is not as dependent on the basis set quality. When the gauge origin is placed on the halogen atom we obtain results in good agreement with the London orbital formalism. To test the sensitivity of the calculated NMR parameters to the nuclear model that was used, we also did the relativistic calculation for HI using a point charge nuclear model for the determination of the zeroth-order wave function. This increased the calculated iodine isotropic shielding parameter by 15 ppm and decreased the isotropic J-coupling parameter by 3.3 Hz. The change in the nuclear model did not affect the calculated hydrogen shielding to the accuracy reported here.

The relativistic effect on the shielding was large and it influenced both the hydrogen and the halo-

**TABLE I.**  
**Isotropic Shieldings of Halogen Halides HX.**

	$\sigma^{\text{NR}}$	$\sigma^{\text{SO}}$	$\sigma^{\text{MC}}$	$\sigma^{\text{NR}+\text{SO}+\text{MC}}$	$\sigma^{\text{Rel}}$
HF (H)	27.73 (28.37)	0.13	−0.02	27.84	27.87
HCl (H)	30.12 (30.62)	0.84	−0.01	30.95	31.00
HBr (H)	30.55 (30.72)	5.58	−0.02	36.12	36.08
HI (H)	31.05 (31.20)	18.38	−0.02	49.41	47.98
HF (F)	414.3 (414.0)	0.3	8.6	423.2	423.3
HCl (Cl)	957.0 (957.3)	2.6	60.5	1020.1	1020.1
HBr (Br)	2634.2 (2634.1)	33.2	543.2	3210.5	3224.6
HI (I)	4541.4 (4541.5)	141.7	1919.1	6602.2	6768.4

The gauge origin is placed at the halogen nucleus.  $\sigma^{\text{NR}}$  is the shielding calculated using the non-relativistic formalism, values in parentheses are obtained using the London orbital formalism.  $\sigma^{\text{SO}}$  is the spin-orbit correction calculated with quadratic response theory (Eq. 3).  $\sigma^{\text{MC}}$  is the scalar relativistic MVEF-FC correction calculated with linear response theory (Eq. 4).  $\sigma^{\text{NR}+\text{SO}+\text{MC}}$  is the shielding calculated with perturbative inclusion of both the spin-orbit and the MVEF-FC correction.  $\sigma^{\text{Rel}}$  is the shielding calculated with the 4-component relativistic RPA method. All values are given in ppm.

gen shielding tensors. The latter was to be expected as the relativistic effects arise mostly from the strong electrostatic potential near the halogen nucleus.

For the hydrogen shielding we found that inclusion of the Breit–Pauli spin-orbit operator in a nonrelativistic calculation brought the nonrelativistic calculation into good agreement with the relativistic result for the hydrogen shielding (Fig. 1). This confirms the findings of Nakatsuji et al.,<sup>5</sup> who use a smaller basis set and the finite field method. We can compare our  $\langle \langle \text{FC}, \text{OZ}, \text{SO} \rangle \rangle$  and  $\langle \langle \text{SD}, \text{OZ}, \text{SO} \rangle \rangle$  isotropic values directly with their values and find good agreement for the FC contribution. If we make the same approximation for the SD contribution as Nakatsuji et al. did (taking only the diagonal terms of the SD tensor operator, fourth column of Table II), we find very good agreement with their SD values as well. This diagonal approximation appears to work well for the hydrogen isotropic shieldings of the lighter members of the series, giving errors that are negligible compared to the other terms. The scalar relativistic MVEF-FC mass-velocity correction is negligible for the hydrogen shieldings, giving values of around −0.02 ppm for all molecules. Because our method of including spin-orbit effects is identical to the one used by Vaara et al.,<sup>15</sup> we should also find good agreement with their HF level results. This is indeed the case with the largest differences occurring for  $\sigma^{\text{NR}}$  (Table I, their table III). When we compare the individual spin-orbit contributions in Table II (their table III), we find that these are less sensitive to the basis set used and are in very good agreement. All methods that include spin-orbit coupling are also qualita-

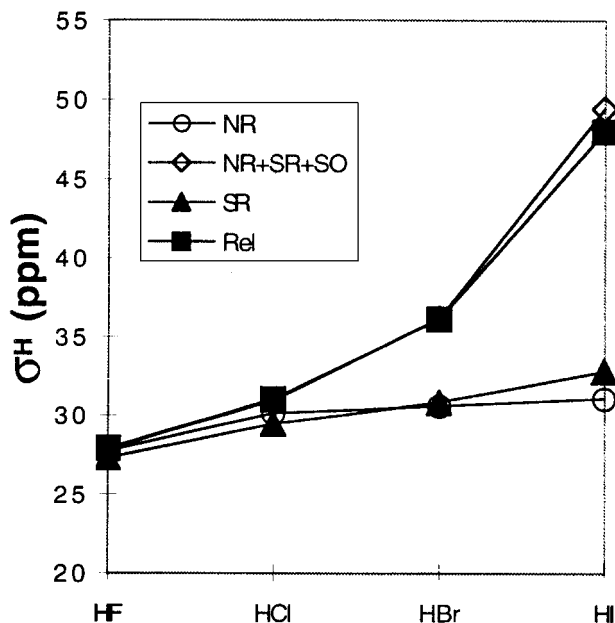
tively in agreement with the experimentally observed trend of increasing hydrogen shielding along the series.

The anisotropy of the hydrogen shielding shows a large relativistic effect that even makes the anisotropy parameter almost zero for HI (Table III, Fig. 2). This trend is also present when the Breit–Pauli spin-orbit operator is included perturbatively. It arises in the latter case because the perturbation correction from  $\langle \langle \text{FC}, \text{OZ}, \text{SO} \rangle \rangle$  on  $\sigma_{\parallel}$  is zero by symmetry, while the correction on  $\sigma_{\perp}$  is large. The MVEF-SD mass-velocity correction is negligible, so the entire effect comes from spin-orbit coupling. The correlated (CASSCF) perturbative calculations of Vaara et al.<sup>15</sup> show a smaller, but still significant, relativistic change of the anisotropy, however, because electron correlation reduces this FC contribution that is largely responsible for the spin-orbit effect on the anisotropy. This means that both our fully relativistic and the perturbative spin-orbit results probably overestimate the relativistic effect due to the neglect of electron correlation. A verification of the general trend in the reduced anisotropy due to relativity by comparing with the experiment is difficult because the “experimental” values are usually obtained by relating measured spin-rotation interaction constants to the paramagnetic part of the shielding tensor. Gierke and Flygare,<sup>36</sup> who introduced this method, combine the experimental spin-rotation data with calculated values of the diamagnetic contribution to obtain an empirical value for the total shielding parameters. An interesting and often overlooked complication is that the paramagnetic contribution to the parallel component of the shielding tensor for linear molecules

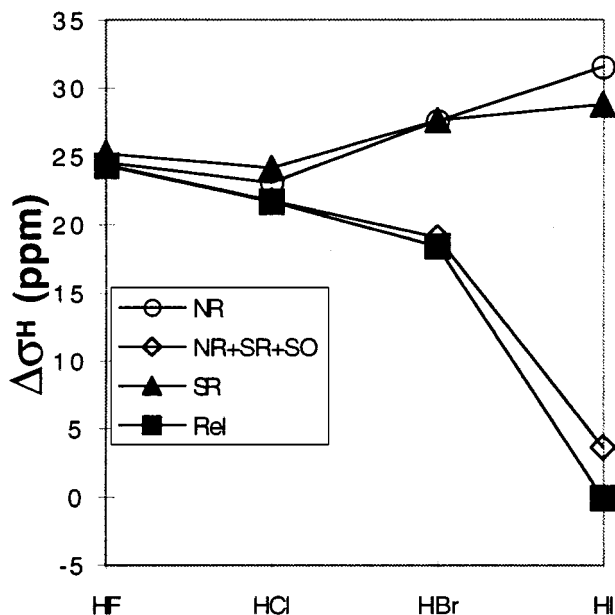
**TABLE II.**  
Isotropic Values of Response Functions that Give Scalar Relativistic and Spin-Orbit Induced Contributions to Isotropic Shieldings of Halogen Halides HX.

	<< FC; MVEF >>>	<< FC; OZ; SO1 >>>	<< FC; OZ, SO2 >>>	<< FC, OZ, SO2 >>>	<< SD; OZ, SO1 >>>	<< SD-D; OZ, SO1 >>>	<< SD; OZ, SO2 >>>
HF (H)	-0.02	0.17	-0.05	0.02	0.02	0.02	-0.01
HCl (H)	-0.01	0.98	-0.18	0.05	0.04	0.04	-0.01
HBr (H)	-0.02	5.96	-0.59	0.24	0.17	0.17	-0.02
HI (H)	-0.02	19.16	-1.28	0.55	0.38	0.38	-0.04
HF (F)	8.56	0.40	-0.17	0.16	0.05	0.05	-0.06
HCl (Cl)	60.46	2.62	-0.70	0.99	0.30	0.30	-0.26
HBr (Br)	543.18	28.78	-3.90	9.93	3.12	3.12	-1.61
HI (I)	1919.11	109.89	-10.51	47.57	13.88	13.88	-5.21

MVEF is the mass velocity external field operator [eq. (4)], FC is the Fermi contact operator, SD the spin-dipolar operator, SD-D the diagonal part of the spin-dipolar tensor operator, OZ the orbital-Zeeman operator for the external magnetic field, SO1 the one-electron spin-orbit operator, and SO2 the two-electron spin-orbit operator. The gauge origin is placed at the halogen nucleus. All values are given in parts per million.



**FIGURE 1.** Isotropic hydrogen shielding parameters (ppm) calculated in the nonrelativistic (NR), nonrelativistic with perturbative inclusion of scalar relativistic effects and spin-orbit coupling (NR + SR + SO), scalar relativistic (SR, ref. 16), and four-component relativistic (Rel) RPA formalisms.



**FIGURE 2.** Anisotropic hydrogen shielding parameters (ppm) calculated in the nonrelativistic (NR), nonrelativistic with perturbative inclusion of scalar relativistic effects and spin-orbit coupling (NR + SR + SO), scalar relativistic (SR, ref. 16), and four-component relativistic (Rel) RPA formalisms.



**TABLE III.**  
**Anisotropy ( $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ ) of Shieldings of Halogen Halides HX.**

	$\Delta\sigma^{\text{NR}}$	$\Delta\sigma^{\text{SO}}$	$\Delta\sigma^{\text{MD}}$	$\Delta\sigma^{\text{NR+SO+MD}}$	$\Delta\sigma^{\text{Rel}}$
HF (H)	24.54 (23.58)	−0.21	0.0135	24.34	24.31
HCl (H)	23.01 (22.26)	−1.30	0.0059	21.71	21.63
HBr (H)	27.53 (27.28)	−8.54	0.0054	19.00	18.33
HI (H)	31.52 (31.29)	−27.91	0.0044	3.62	−0.13
HF (F)	100.9 (101.4)	0.3	−0.0022	101.2	100.04
HCl (Cl)	287.7 (287.2)	1.3	−0.0155	289.0	281.60
HBr (Br)	738.1 (738.2)	5.3	−0.0287	743.4	663.76
HI (I)	1446.2 (1446.0)	11.4	−0.0451	1457.5	1032.3

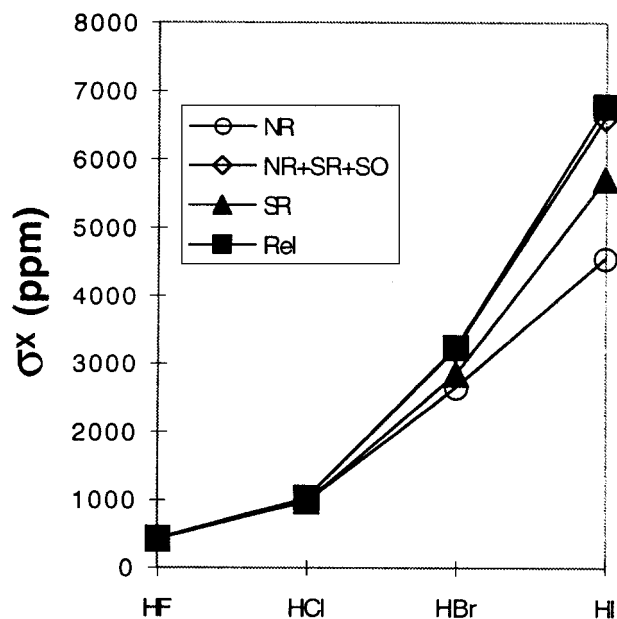
The gauge origin is placed at the halogen nucleus.  $\Delta\sigma^{\text{NR}}$  is calculate using the non-relativistic formalism, values in parentheses are obtained using the London orbital formalism.  $\Delta\sigma^{\text{SO}}$  is the spin-orbit correction calculated with quadratic response theory [eq. (3)].  $\Delta\sigma^{\text{NR+MD}}$  is the scalar relativistic MVEF-SD correction calculated with linear response theory [eq. (4)].  $\Delta\sigma^{\text{NR+SO+MD}}$  is the shielding calculated with perturbative inclusion of both the spin-orbit and the MVEF-SD correction.  $\Delta\sigma^{\text{Rel}}$  is calculated with the four-component relativistic RPA method. All values are given in ppm.

is not zero in a relativistic formalism.<sup>4</sup> This makes the extracted experimental values of the anisotropy parameters unreliable, especially for heavier elements where the neglected contribution to the parallel component can become as large as the perpendicular components.

Fukui and Baba<sup>16</sup> found a scalar relativistic effect on the hydrogen shielding that strongly depends on the gauge origin used in the calculations. For both choices of gauge origin (on the hydrogen and on the halogen nucleus) for which they report shieldings, the scalar relativistic effect is much larger than the MVEF-FC mass-velocity correction (FC-IV) that we calculate using Fukui's original idea. Another difference is that they also found a significant scalar relativistic effect on the anisotropy while the anisotropic MVEF-SD correction formulated in eq. (4) is negligible compared to the other contributions. Despite these significant discrepancies, the absolute magnitude of the scalar relativistic effect is in both approaches small compared to the spin-orbit effect. The same conclusion is reached when comparing the scalar relativistic and spin-orbit DFT calculations of the Ziegler group.<sup>19,20</sup> We therefore conclude that for the hydrogen shielding, the distortion of the electronic wave function due to spin-orbit coupling dominates and that the scalar relativistic effect is small.

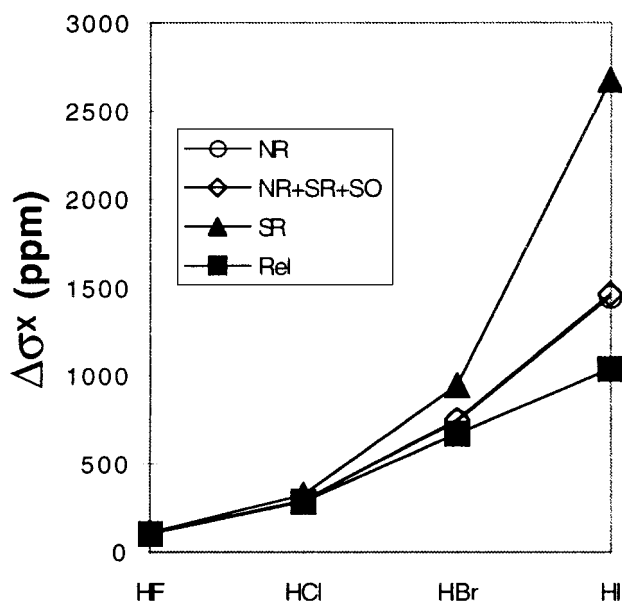
For the halogen atom shielding we found, as might be expected, a much larger relativistic effect. The perturbative spin-orbit calculations showed that in this case the SD term is no longer small compared to the FC term. Furthermore, the diagonal approximation for the SD contribution now gives large deviations from the full result. The spin-orbit effect alone does not explain the differ-

ence between the relativistic and nonrelativistic results for the halogen shielding. Inclusion of the MVEF-FC correction is necessary in this case and brings the isotropic shielding parameter in surprisingly good agreement with the full four-component result, especially for the fluorine and chlorine shieldings (Fig. 3). Using the Douglas–Kroll approach, Fukui and Baba<sup>16</sup> also report a sizable scalar relativistic effect that does not vary much



**FIGURE 3.** Isotropic halogen shielding parameters (ppm) calculated in the nonrelativistic (NR), nonrelativistic with perturbative inclusion of scalar relativistic effects and spin-orbit coupling (NR + SR + SO), scalar relativistic (SR, ref. 16), and four-component relativistic (Rel) RPA formalisms.

with the choice of gauge origin. Their calculated isotropic shielding parameters are, however, halfway between the nonrelativistic and fully relativistic result, which may be due to their neglect of picture change. When we calculated the anisotropy on basis of their reported values for  $\sigma_{\parallel}$  and  $\sigma_{\perp}$ ; we found that the deviation from the nonrelativistic value was opposite in sign to the full relativistic correction (see Fig. 4). The spin-orbit effect on the anisotropy is, contrary to that observed in the hydrogen shieldings, relatively small and also of opposite sign to the full relativistic correction. The scalar relativistic MVEF-SD correction to the anisotropy is also small and does not explain the



**FIGURE 4.** Anisotropic halogen shielding parameters (ppm) calculated in the nonrelativistic (NR), nonrelativistic with perturbative inclusion of scalar relativistic effects and spin-orbit coupling (NR + SR + SO), scalar relativistic (SR, ref. 16), and four-component relativistic (Rel) RPA formalisms.

full relativistic shift. It thus appears that separate calculations of scalar relativistic and spin-orbit effects may only be possible for the isotropic shieldings and that the interplay between the two effects is important to obtain a reliable value of the anisotropy.

## INDIRECT NUCLEAR SPIN-SPIN COUPLINGS

The calculated spin-spin couplings are best discussed using the reduced coupling constants  $K$  (Table IV). We see a large difference between the relativistic and nonrelativistic values for HBr and HI. The trend of decreasing coupling constants going from HF to HI that is found also in the nonrelativistic calculations is greatly enhanced by relativistic effects. The nonrelativistic result is calculated as the sum of three response functions of which the FC interaction is the largest term. Contrary to the shieldings, no new nuclear magnetic operators are introduced upon including the spin-orbit coupling operator because  $H^{FC}$  and  $H^{SD}$  do already contribute in second order, and most of the attention has been focused on correction of the FC contribution. The  $B(n, Z)$  scaling factors proposed by Breit<sup>37</sup> can be used to scale the FC term by a factor representing the relativistic contractions of the s orbitals on both nuclei.<sup>18</sup> This gives a simple estimate of the scalar relativistic effects that works surprisingly well in cases where the spin-spin coupling parameter is dominated by the FC term. Applying these scaling terms (tabulated by Pyykkö et al.<sup>17</sup>) to our nonrelativistically calculated FC contribution (assuming that this contribution arises completely from the outermost s functions in the molecule so that we can use the scaling parameter for this function to the final value of the FC contribution) does not bring the nonrelativistic results into agreement with the relativistic results for the molecules considered here. The spin-orbit

**TABLE IV.**  
**Isotropic (Reduced) Indirect One-Bond Spin – Spin Coupling of Halogen Halides HX.**

Molecule	${}^1K_{HX}^{FC}$	${}^1K_{HX}^{NR}$	${}^1K_{HX}^{NR-FCS}$	${}^1K_{HX}^{Rel}$	${}^1J_{HX}^{NR}$	${}^1J_{HX}^{Rel}$
${}^1H^{19}F$	37.57	54.15	54.50	53.99	612.23	610.42
${}^1H^{35}Cl$	15.75	27.46	27.99	26.27	32.36	30.95
${}^1H^{79}Br$	-13.92	4.81	2.68	-15.82	14.52	-47.76
${}^1H^{127}I$	-32.74	-12.97	-26.20	-113.20	-31.38	-273.94

The constants were calculated in the nonrelativistic (NR), nonrelativistic with a scaled Fermi contact contribution (NR-FCS, ref. 16), and four-component relativistic (Rel) RPA formalisms. The (unscaled) Fermi contact contribution to the reduced coupling constant is also given separately in the second column. The reduced coupling constant  $K$  is given in  $10^{19} T^2 J^{-1}$ ; the coupling constant  $J$  is given in Hertz.

effect was calculated by Kirpekar et al.<sup>14</sup> for the methane analogues where they found that for  $\text{SnH}_4$  the effect is only 1% of the total  $J_{\text{Sn-H}}$  value, indicating that the pure spin-orbit correction to couplings may be a small fraction of the total relativistic correction for other molecules. This may also explain the small relativistic effect on the anisotropy parameters that is due to the fact that both  $J_{\parallel}$  and  $J_{\perp}$  are reduced by the same amount from scalar relativistic effects (Table V). If this is the case one may hope to obtain a reasonable estimate of the relativistic correction by a more sophisticated scalar relativistic method than the scaling that we used above. However, to obtain a reliable value one should also consider electron correlation because this is known to be important for the indirect spin-spin couplings and tends to reduce the magnitude of the calculated  $J$  tensor.

## Conclusions

For the calculation of hydrogen shieldings inclusion of the Breit–Pauli spin-orbit operator in an analytic perturbation theory approach or inclusion of the Douglas–Kroll spin-orbit operator in a variational approach gives most of the relativistic effect on the isotropic shielding constants. The dominant term is the one-electron spin-orbit interaction coupled to the FC interaction. The two-electron spin-orbit interaction term and the SD terms are less than 10% thereof for HBr and HI. This also indicates that the neglect of the Breit interaction in the four-component calculations does not give rise to large errors because it only modifies the two-electron contribution. For the heavy atom shielding spin-orbit coupling included to first order gives only part of the relativistic effect and a method that includes scalar relativistic effects is necessary. A good first approximation appears to be the use of the MVEF-FC term in second-order perturbation theory. The success of this approach is rather sur-

prising because the MVEF term is only one of the terms that arise from expansion of the mass-velocity operator. In the same order in the magnetic field one will also find corrections to the internal-field operators, as well as to the external-field orbital Zeeman operator. The corrections to the internal-field operators were discarded simply because they are singular within the Breit–Pauli approximation, which of course does not mean that a regularized form of these corrections would not be important.

Given the magnitude of the relativistic correction for hydrogens bonded to the heavier halogens and the good agreement between the fully relativistic and the perturbative calculations, we recommend routine inclusion of the one-electron term in hydrogen shielding calculations in compounds that contain heavy elements to obtain a reasonable estimate of the relativistic effect. Adding the two-electron terms will increase the precision but will also increase the computational cost dramatically. In that case one might as well resort to the four-component approach directly because the total timings of the calculations are comparable. We furthermore recommend routine inclusion of both the one-electron spin orbit and the MVEF-FC [defined in eqs. (4) and (4a)] relativistic corrections for heavy atom shieldings.

The spin-spin coupling tensor calculated in a nonrelativistic formalism cannot be corrected easily for the large relativistic effects that we found. Inclusion of the spin-orbit operator in a perturbative way does not give rise to additional contributions from the internal magnetic field operators, and application of the simple FC scaling procedure to approximate the scalar relativistic effect does not improve the nonrelativistic results much.

The neglect of electron correlation in our calculations makes direct comparison with experiments difficult. Adding our calculated relativistic correction to a correlated nonrelativistic calculation could therefore be considered as a possible route to im-

**TABLE V.**  
**Anisotropies of Indirect One – Bond Spin – Spin Coupling Constants of Halogen Halides HX.**

Molecule	$\Delta^1 K_{\text{HX}}^{\text{NR}}$	$\Delta^1 K_{\text{HX}}^{\text{Rel}}$	$\Delta^1 J_{\text{HX}}^{\text{NR}}$	$\Delta^1 J_{\text{HX}}^{\text{Rel}}$
$^1\text{H}^{19}\text{F}$	14.03	14.17	158.68	160.19
$^1\text{H}^{35}\text{Cl}$	70.84	71.40	83.47	84.13
$^1\text{H}^{79}\text{Br}$	206.10	216.29	622.39	653.18
$^1\text{H}^{127}\text{I}$	340.17	369.82	823.20	894.95

The constants were calculated in the nonrelativistic (NR) and four-component relativistic (Rel) RPA formalisms. The reduced coupling constant  $\Delta K$  is given in  $10^{19} \text{T}^2 \text{J}^{-1}$ ; the coupling constant  $\Delta J$  is given in Hertz.

prove the results. A warning is in place here. For the shieldings we may assume that the effect of electron correlation is relatively small like the effect found when comparing the quadratic response Monte Carlo SCF calculations of Vaara et al.<sup>15</sup> with their HF level calculations so that such a simple additive scheme could work. A complication is, however, that experimental shielding values may be wrong because it has often been erroneously assumed that the parallel component of the shielding tensor for linear molecules is also zero in the relativistic case.

For the spin–spin couplings electron correlation in general tends to be more important and most often reduces the size of the expected relativistic effect. Work on a relativistic correlated approach that is capable of handling magnetic field perturbations is planned and it would provide a reliable way of obtaining the relativistic and electron correlation contributions.

The use of a four-component relativistic formalism becomes a good alternative to the perturbational approaches because of its ease of application. The spin–spin couplings and the shieldings can both be calculated via one type of response function each. This is also the case for the nonrelativistic calculation of NMR shieldings but, as shown above, when one needs to include spin-orbit coupling this is no longer true and a number of additional response functions needs to be calculated, even when restricting oneself to first-order perturbation theory. This is more complicated and generally computationally more expensive than the direct relativistic calculation.

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